

# Synthesis of kaolinite-filled EPDM rubber composites by solution intercalation: structural characterization and studies on mechanical properties

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**Abstract** In the large field of nanotechnology, polymer matrix-based nanocomposites have become a prominent area of current research and development. Exfoliated clay-based nanocomposites have dominated the polymer world with excellent characteristics. EPDM rubber composites have been synthesized by solution-intercalation using the easily available kaolinite as filler. The composite structure has been elucidated by X-ray diffraction (XRD), Fourier transform IR, and scanning electron microscope studies. The molecular level dispersion of clay layers has been verified by the disappearance of basal XRD peak of kaolinite in the EPDM/kaolinite composites. The mechanical properties showed significant improvement of EPDM/kaolinite composites with respect to neat EPDM.

**Keywords** EPDM · Kaolinite · Solution-intercalation · Morphology · Mechanical properties

## Introduction

In the growing field of nanotechnology, polymer-matrix based nanocomposites have become a prominent area of current research and development. Reinforcing polymer matrices with fillers proves to be an effective tactics which will result in nanocomposites tailor-made for specific applications. Polymer composites are formed when phase-mixing of effective fillers occurs within the polymer matrix. Due to the improved phase morphology and

interfacial properties, composites exhibit mechanical, thermal, barrier, and chemical properties superior to conventional polymers based on the fillers used (Giannelis 1996; Lan and Pinnavaia 1994; Uhl and Wilkie 2002; Agag et al. 2001; Messersmith and Giannelis 1993; Kojima et al. 1993; Usuki et al. 1993). Kaolinite, the most prominent clay material available in South India, is part of the group of industrial minerals, with the chemical composition  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Chemical modification of layered silicates has been previously reported through an ion-exchange reaction with  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and organic cations such as alkyl ammonium ions to form the organo-silicate (Whittingham and Jacobson 1982). Exfoliated nanocomposites are obtained when the nanokaolin clay platelets are dispersed in the polymer matrix.

Ethylene propylene diene monomer (EPDM) is an unsaturated polyolefin rubber with a wide range of applications. Due to the absence of any polar groups on the backbone of EPDM, it is incompatible with the polar organophilic clay. Recent works have reported preparation of non-polar polymers clay-hybrids using functional oligomers (Kawasumi et al. 1997; Kato et al. 1997; Hasegawa et al. 1998; Hasegawa et al. 2000). Usukai et al. (2002) and Chang et al. (2002), respectively, have studied the mechanical properties of EPDM-clay nanocomposites, prepared via the vulcanization process using some special vulcanization accelerators and the melt compounding process with a liquid-low molecular weight EPDM. Not many reports are available for EPDM-clay matrices prepared using solution-intercalation especially kaolinite as filler.

In the present work, EPDM-kaolinite composites have been prepared by solution-intercalation method using

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dicumyl peroxide as curing agent and the morphology of the composites studied using FT-IR, W-XRD, and SEM techniques. The mechanical properties of EPDM reinforced with kaolinite and virgin EPDM have also been compared.

## Experimental

### Materials

EPDM rubber sample pack was obtained from Dupont–Dow. Kaolinite powder with 20–50  $\mu\text{m}$  average thickness was obtained as an industrial product from SanXing High-New Material Company of Zaozhuang in China. Toluene and xylene were supplied by CDH, New Delhi. Double distilled water was used throughout the study.

### Preparation of EPDM/CA-MMT nanocomposites

Varying amount of kaolinite (1, 3, 5 and 7 phr) was added to EPDM rubber (16 g) dissolved in toluene (300 mL) in a three-necked flask (500 mL) and ultrasonicated for perfect dispersion. The contents were mechanically stirred for 5 h at 60°C, cured by adding dicumyl peroxide (3 phr) just

4–5 min before completion of heating and immediately transferred into glass moulds when thin films of the nanocomposite were obtained, by dipping the mould into water, after extracting the solvent.

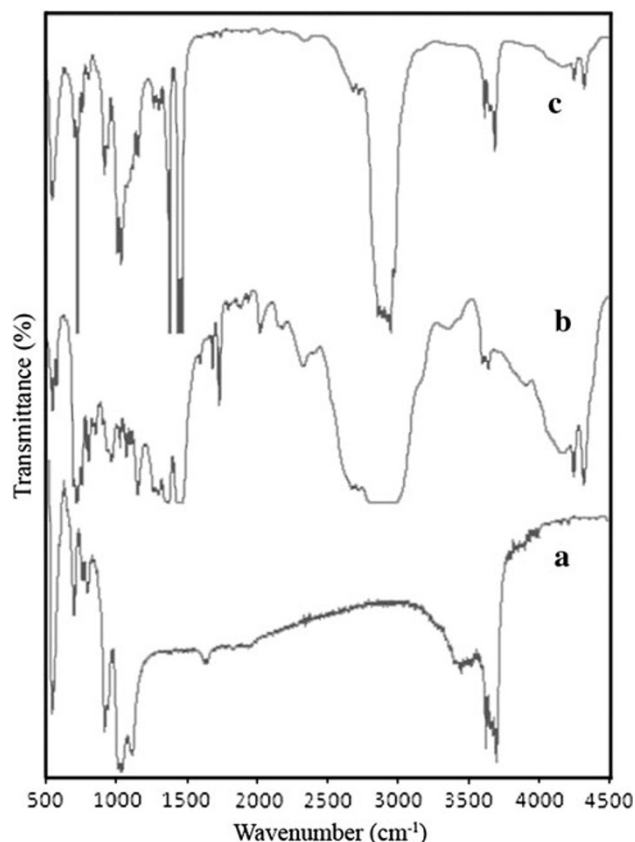
### Characterization

The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet spectrophotometer model Nexus-670 in the range of 400–4,500  $\text{cm}^{-1}$ . X-ray diffraction patterns were obtained using an X-Pert pro diffractometer, with Cu K $\alpha$  radiation. Tensile tests were performed using INSTRON 3365, UK, as per ASTM-D3039 standards with a cross head speed of 100 mm  $\text{min}^{-1}$ . The surfaces were coated with gold and examined under a scanning electron microscope (CARL-ZEISS, Model EVO-50).

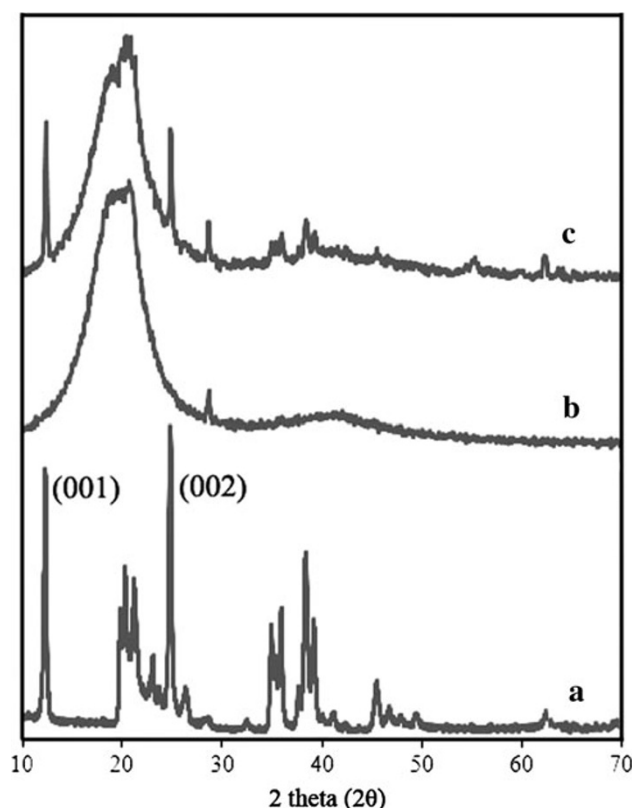
## Results and discussion

### Morphological studies

The morphological studies were performed using FT-IR, XRD and SEM techniques. Figure 1 depicts the IR spectra of kaolinite (1a), EPDM (1b) and kaolinite-filled EPDM



**Fig. 1** FT-IR spectra of **a** kaolinite, **b** EPDM, and **c** kaolinite-filled EPDM



**Fig. 2** XRD patterns of **a** kaolinite, **b** EPDM, and **c** kaolinite-filled EPDM

(1c). The peak at  $3,620\text{ cm}^{-1}$  refers to the inner O–H stretching, while the  $3,710\text{ cm}^{-1}$  peak corresponds to the in-phase stretching of the three inner-surface O–H groups, and the signals at  $3,669$  and  $3,652\text{ cm}^{-1}$  are due to the anti-phase stretching modes of the inner-surface O–H groups. The absorption at  $1,008$  and  $1,032\text{ cm}^{-1}$  could be attributed to the anti-symmetric stretch of equatorial Si–O bonds (Etienne Balan et al. 2001). The in-phase stretch of apical Si–O bonds appears on the spectrum at  $1,134\text{ cm}^{-1}$  and the band at  $1,090\text{ cm}^{-1}$  corresponds to the symmetric stretch of equatorial Si–O bonds. The absorption band at  $1,090\text{ cm}^{-1}$  is characteristic of kaolinite. After processing, kaolinite-filled EPDM exhibited the characteristic bands at  $1,090$  and  $3,710\text{ cm}^{-1}$  which were absent in the virgin EPDM. This confirms the presence of kaolinite layers within EPDM matrix. Also, the difference in absorption of virgin EPDM and kaolinite-filled EPDM at  $2,700\text{--}3,000\text{ cm}^{-1}$  shows a definite morphological change.

Figure 2 depicts the X-ray profile of kaolinite (2a), EPDM (2b), and the kaolinite-filled EPDM (2c). The basal spacing of (001) and (002) planes are  $7.214 \times 10^{-1}$  and  $3.587 \times 10^{-1}\text{ nm}$ , respectively, showing the characteristic peaks of kaolinite in Fig. 2a, c. The absence of other characteristic diffraction peaks of kaolinite in Fig. 2c

between  $20^\circ\text{--}25^\circ$  and  $35^\circ\text{--}40^\circ$  goes to prove the special directional and parallel arrangements of kaolin platelets within the rubber matrix, consistent with the dispersed pattern observed from the SEM technique. Further, the EPDM polymer has also intercalated between the layers of the kaolinite as shown by the increase in d-spacing with the consequent shifting of  $2\theta$  value ( $24.97\text{--}24.73$ ) (Qinfu Liu et al. 2008).

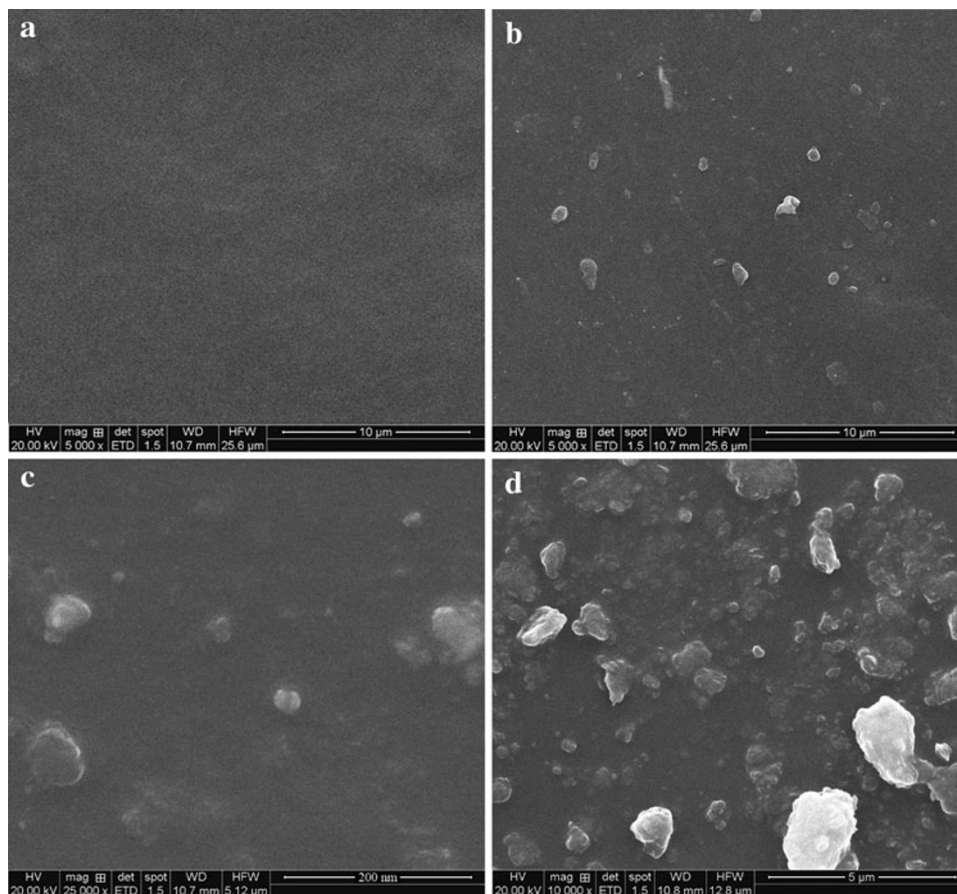
SEM images given in Fig. 3 clearly depict the even distribution of clay particles in the matrix and also the possible clay layers in nano-scale with a little agglomeration.

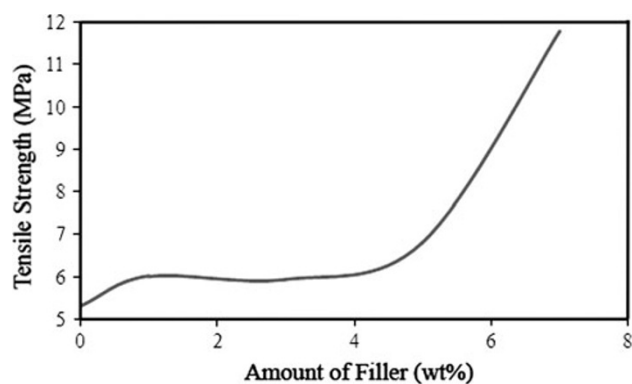
### Mechanical properties

The mechanical testing was performed on the EPDM/kaolinite clay matrices under different filler content and the variation in tensile strength (Fig. 4) shows that there is a small increase of tensile strength until 3% clay content and thereafter gets doubled for 7% kaolinite-filled composites. The 7% clay-filled matrix has shown more than a twofold increase in tensile strength compared to the neat EPDM.

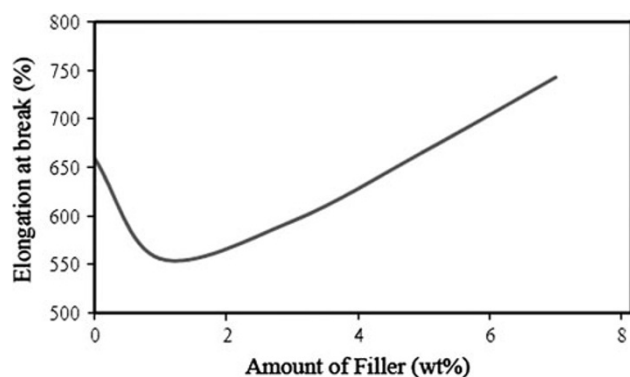
Figure 5 shows the effect of filler content on elongation at break. Elongation at break of the EPDM films initially

**Fig. 3** SEM images of **a** virgin EPDM, **b** 1 wt% kaolinite-filled EPDM, **c**, **d** 5 wt% filled EPDM

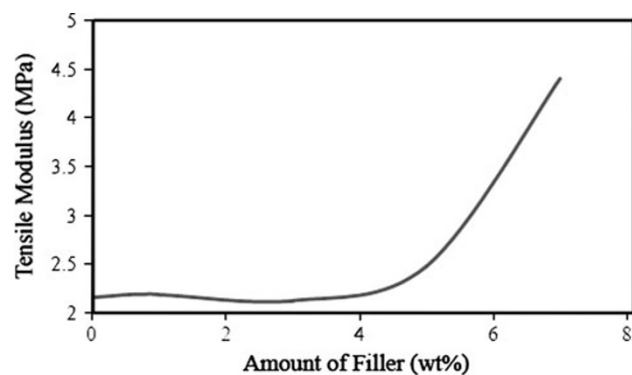




**Fig. 4** Tensile strength versus amount of kaolinite



**Fig. 5** Elongation at break versus amount of kaolinite



**Fig. 6** Tensile modulus versus amount of kaolinite

decreases with kaolinite content and then shows a steady increase. This increase may be attributed to the possible intercalation of the rubber polymer chains within the clay matrices.

The tensile modulus of the composites also shows a similar scenario as that of the tensile strength (Fig. 6). The enhancement in tensile strength and tensile modulus is the direct manifestation of the dispersion of kaolinite layers in the EPDM matrix and the strong interaction between EPDM and kaolinite clay (Seyed Javad Ahmadi et al. 2005)

is further confirmed by the increased d-spacing in the XRD patterns of the EPDM/kaolinite composites.

Comparing this result to the mechanical properties of cetyl ammonium modified montmorillonite (CA-MMT) filled EPDM obtained in our previous work, the tensile strength of 5% CA-MMT filled EPDM is 11.17 MPa which is attained here by 7% kaolinite filled EPDM. The tensile modulus of 5 wt% CA-MMT-filled EPDM is 3.37 but those of 5 and 7% kaolinite filled EPDM are 2.48 and 4.41, respectively.

## Conclusion

The morphological studies of the EPDM/kaolinite composites indicate the uniform dispersal of the clay particles with possible intercalation of clay layers. The kaolinite composites have superior mechanical properties compared to those of the neat resin. The enhanced characteristics are attributed to the uniform dispersal of the clay particles in the polymer matrix. Reinforcing higher proportion of kaolinite in the polymer matrix could match the high quality of MMT-filled EPDM vis-à-vis the mechanical properties. The abundance of kaolinite in this part of the country could be an efficient substitute in chosen aspects of using MMT clay as filler in polymer matrices.

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